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<b>(21) International Application Number:</b> PCT/US95/16013 <b>(22) International Filing Date:</b> 20 December 1995 (20.12.95)  <b>(30) Priority Data:</b> 08/366,189 29 December 1994 (29.12.94) US 08/457,932 1 June 1995 (01.06.95) US  <b>(71) Applicant:</b> HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).  <b>(72) Inventors:</b> ARORA, Kartar, S.; 106 Harrison Forge Court, Chalfont, PA 18914 (US). WIGGINS, Michael, S.; 2405 Hillock Court, Lansdale, PA 19446 (US).  <b>(74) Agent:</b> GRANDMAISON, Real, J.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SELF-DISPERSING CURABLE EPOXY RESIN DISPERSIONS AND COATING COMPOSITIONS MADE THEREFROM  <b>(57) Abstract</b>  There is disclosed a self-dispersing curable epoxy resin composition comprising the addition product of reactants comprising (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.1 to 1.0 reactive equivalents of a polyhydric phenol and (c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct comprising the addition product of reactants comprising 1.0 reactive equivalents of a polyepoxide and from about 0.3 to 0.9 reactive equivalents of a polyoxyalkyleneamine containing monosubstituted ethoxy groups.		

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SELF-DISPERSING CURABLE EPOXY RESIN  
DISPERSIONS AND  
COATING COMPOSITIONS MADE THEREFROM

Cross-Reference to Related Applications

This application is a continuation-in-part of pending U.S. Patent Application No. 08/366,189 filed December 29, 1994.

Field Of The Invention

5           The present invention relates to a method of making aqueous epoxy resin dispersions. The dispersions are useful in preparing coating compositions comprising the same.

Background of the Invention

10           Epoxy resins have come into widespread use as components in coating compositions. Coatings which comprise cured epoxy resins are valued for their durability, chemical resistance, and excellent adhesion to a

broad range of substrates. Particularly desirable from an environmental point of view are epoxy resins which may be applied to a substrate with either minimal or no release of volatile organic components. Toward this end, there has been much research directed to the development of

5 aqueous dispersions and emulsions of epoxy resins.

One class of aqueous epoxy dispersions employs one or more additives, also known as dispersants or emulsifiers or surfactants, which are necessary to stabilize the epoxy resin in the dispersion or emulsion form. Representative examples include an aqueous epoxy dispersion as

10 described in U.S. Patent No. 3,301,804 (employing the reaction product of a boric acid ester derived from boric acid with both an alkylene glycol and a beta-dialkyl-substituted aminoalkanol as an emulsifier), U.S. Patent No. 3,634,348 (employing a phosphate ester as an emulsifying agent), U.S. Patent No. 3,249,412 (employing in combination a cationic emulsifying

15 agent selected from the group consisting of imidazolines and amides and a non-ionic emulsifying agent), and Specialty Chemicals Bulletin SC-021 titled "Water-Reducible Coatings via Epoxy Resin Modification with Jeffamine (Reg. TM) ED-2001 and Jeffamine (Reg. TM) M-1000" available from Texaco Chemical Company, Bellaire, Texas. Another example

20 comes from the technical literature of Synthron Inc., Morgantown, North Carolina, which discloses the use of PROX-E-141, a diglycidyl ether of Pluronic (Reg. TM) F88 diol (an ethylene oxide - propylene oxide - ethylene oxide block copolymer available from BASF Performance

Chemicals, Parsippany, New Jersey) as a reactive dispersant for epoxy resins. PROX-E-141 can act as a dispersant for epoxy resin in water, but then will react along with the epoxy resin when exposed to an amine functional curing agent.

- 5           The use of an additive to provide stability to an aqueous epoxy dispersion is preferably avoided as such additives add additional cost, formulation complexity, and may potentially interfere with the performance of a coating derived from the aqueous epoxy dispersion.

          It is known to prepare aqueous epoxy dispersions from self-emulsifying epoxy resins. For example, U.S. Patent No. 4,315,044 describes a stable epoxy dispersion composition comprising (1) an aqueous medium; and (2) between about 50-70 weight percent of self-emulsifying epoxy resin which is the addition product of reactants comprising (a) 40-90 parts by weight of diglycidyl ether of dihydric phenol, (b) 5-35 parts by weight of dihydric phenol, and (c) 2-15 parts by weight of diglycidyl ether of polyoxyalkylene glycol, wherein the molecular weight of the epoxy resin is in the range between about 500-20,000. The dispersion can also contain 1-25 weight percent based on resin solids of a water-immiscible C<sub>8</sub>-C<sub>20</sub> aliphatic monoepoxide reactive diluent.

- 20           U.S. Patent No. 4,608,406 describes stable aqueous epoxy resin dispersions comprised of (1) an aqueous medium; and (2) between about 50 to about 70 weight percent of self-emulsifying epoxy resin which is the addition reaction product of (a) 40-90 parts by weight of a diglycidyl ether

of a dihydric phenol; (b) 5-35 parts of a dihydric phenol; (c) 2-15 parts by weight of a diglycidyl ether of a polyoxyalkylene glycol; and (d) 2 to 15 parts by weight of an alkyl phenol-formaldehyde novolac resin wherein the molecular weight of the epoxy resin is in the range of about 1000 to about 5 20,000. The stable dispersions can be modified by the addition of about 1 to about 25 weight percent of an aliphatic monoepoxide reactive diluent.

In an attempt to improve freeze-thaw stability, the stable aqueous epoxy resin dispersions can be modified by the addition of about 5-20 weight percent, based on resin solids weight, of a water-miscible solvent 10 which, preferably, is a 2 to 8 carbon glycol or glycol ether.

There remains a need for further improvements in terms of the freeze-thaw resistance of aqueous epoxy resin dispersions, and in terms of the corrosion resistance and chemical resistance of coatings derived from aqueous epoxy resin dispersions which are adapted for application as 15 industrial maintenance coating systems.

Accordingly, it is a primary object of this invention to provide a self-dispersing curable epoxy resin which may be dispersed in water without the necessity for an additive to stabilize the epoxy dispersion.

Another object of this invention is to provide aqueous dispersions of 20 self-dispersing curable epoxy resins which exhibit long term stability under ambient storage conditions.

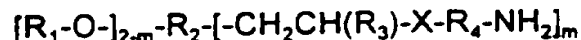
Yet another object of this invention is to provide coating compositions incorporating a self-dispersing curable epoxy resin, where

the coating composition exhibits excellent properties when cured.

Other objects and advantages of the present invention shall become apparent from the accompanying description and examples.

## 5 Summary of the Invention

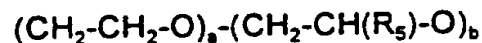
According to the present invention, we disclose a self-dispersing curable epoxy resin composition comprising the addition product of reactants comprising (a) 1.0 reactive equivalent of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents of a polyhydric phenol, and (c) from about 0.005  
10 to 0.5 reactive equivalents of an amine-epoxy adduct comprising the addition product of reactants comprising 1.0 reactive equivalent of a polyepoxide and from about 0.3 to 0.9 reactive equivalents of a polyoxyalkyleneamine having the structural formula:



15 wherein:

$R_1$  designates a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_{12}$  aliphatic, alicyclic or aromatic hydrocarbons, and

$R_2$  represents a polyoxyalkylene chain having the structural formula:



20 wherein:

$R_5$  is a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons,

'a' designates a number of ethoxy groups  $(CH_2-CH_2-O)$ ,

'b' designates a number of monosubstituted ethoxy groups ( $\text{CH}_2\text{-CH(R}_3\text{)O}$ ) where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'a' and 'b' is equal to or greater than 10 but  
5 less than or equal to 200, and where the sequence of ethoxy and monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups,

$\text{R}_3$  designates H or a monovalent organic radical selected from the  
10 group consisting of  $\text{C}_1$  to  $\text{C}_4$  aliphatic hydrocarbons,

$\text{R}_4$  designates aliphatic, cycloaliphatic or aromatic radical containing 6 to 18 carbon atoms and X is  $\text{OC(O)NH}$ ,

and m is equal to 1 or 2.

## 15 Detailed Description of the Invention

The self-dispersing curable epoxy resin used as a starting material herein can be any one of several self-dispersing curable epoxy resins that are based upon a polyoxyalkyleneamine (I).

In certain embodiments, the self-dispersing curable epoxy resin  
20 based on said polyoxyalkyleneamine is prepared by reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents (e.g. from about 0.4 to about 0.6 reactive equivalents or from about 0.65 to about 0.95 reactive equivalents) of a polyhydric phenol, and



(c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct, wherein the amine-epoxy adduct is formed upon contacting 1.0 equivalents of a polyepoxide and from about 0.3 and 0.9 reactive equivalents of a polyoxyalkyleneamine (I). Such self-dispersing curable epoxy resins are similar to those described in detail in U.S. Serial No. 08/255,732, filed June 14, 1994, which is a continuation-in-part of U.S. Serial No. 08/086,288, filed June 30, 1993, and U.S. Serial No. 08/203,543, filed March 1, 1994, the disclosures of which are incorporated herein by reference. The polyoxyalkyleneamine (I) used in present invention is different from that used in U.S. Serial No. 08/255,732, filed June 14, 1994, which is a continuation-in-part of U.S. Serial No. 08/086,288, filed June 30, 1993, and U.S. Serial No. 08/203,543, filed March 1, 1994.

In other embodiments, the epoxy resin is prepared by reacting an epoxy resin with a polyoxyalkyleneamine (I) having a molecular weight of from about 3,000 to about 15,000 in a ratio of about 0.001 to 0.060 reactive equivalents of polyoxyalkyleneamine (I) to about 1.0 reactive equivalents of epoxy resin. Such self-dispersing curable epoxy resins are similar to those described in detail in U.S. Serial No. 08/173,455, filed December 27, 1993, the disclosure of which is incorporated herein by reference. The polyoxyalkyleneamine (I) used in the present invention is different from that used in U.S. Serial No. 08/173,455, filed December 27, 1993.

### The Polyoxyalkyleneamine (I)

The polyoxyalkyleneamine (I) reactant comprises one or more adducts of a monoether of polyoxyalkylenediol or polyoxyalkylenediol and a diisocyanate where the adduct comprises both amine groups and

5 substantially water-soluble polyether chains. The polyoxyalkyleneamine (I) reactant is soluble or at least partially soluble in water.

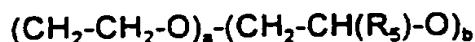
Polyoxyalkyleneamines (I) of this invention have the structural formula:



10 wherein

$R_1$  designates a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_{12}$  aliphatic, alicyclic or aromatic hydrocarbons, and

$R_2$  represents a polyoxyalkylene chain having the structural formula:



15 wherein

$R_5$  is a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons,

'a' designates a number of ethoxy groups  $(CH_2-CH_2-O)$ ,

'b' designates a number of monosubstituted ethoxy groups  $(CH_2-CH(R_5)-$

20  $O)$  where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'a' and 'b' is equal to or greater than 10 but less than or equal to 200, and where the sequence of

ethoxy and monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups, and where the a:b ratio is greater than 1:1.

- 5             $R_3$  designates H or a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons.

$R_4$  is an aliphatic, cycloaliphatic or aromatic group containing 6 to 18 carbon atoms and X is equal to  $OC(O)NH$ .

And m is equal to 1 or 2.

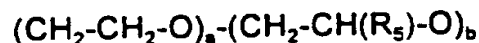
- 10           The polyoxyalkyleneamines suitable for this invention can be obtained from monoethers of polyoxyalkylene diols or polyoxyalkylene diols and diisocyanates. Suitable mono ethers of polyoxyalkylenediols or polyoxyalkylenediols have the structural formula



- 15           wherein

$R_1$  designates a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_{12}$  aliphatic, alicyclic or aromatic hydrocarbons, and

$R_2$  represents a polyoxyalkylene chain having the structural formula:



- 20           wherein

$R_5$  is a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons,

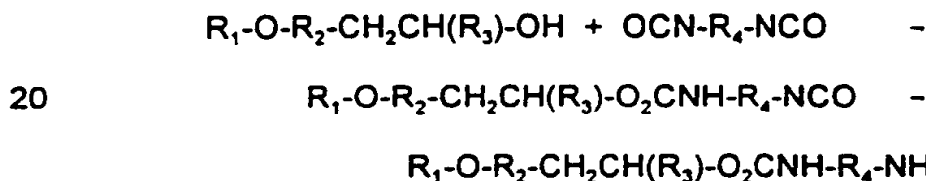
'a' designates a number of ethoxy groups  $(CH_2-CH_2-O)$ ,

'b' designates a number of monosubstituted ethoxy groups (CH<sub>2</sub>-CH(R<sub>5</sub>)-O) where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'a' and 'b' is equal to or greater than 10 but less than or equal to 200, and where the sequence of ethoxy and monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups, and where the ratio of a:b is greater than 1:1.

10           R<sub>3</sub> designates H or a monovalent organic radical selected from the group consisting of C<sub>1</sub> to C<sub>4</sub> aliphatic hydrocarbons.

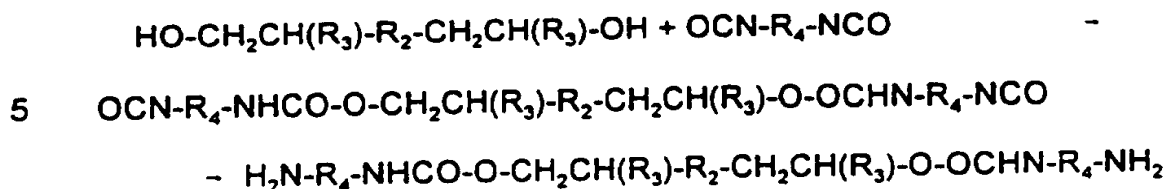
And m is equal to 1 or 2.

Techniques to prepare suitable mono ethers of polyoxyalkylene diols are known in the art, and include reacting a hydroxyl group containing initiator with ethylene oxide and/or propylene oxide. The mono ether of polyoxyalkylene diol is reacted with a diisocyanate to form an isocyanate terminated adduct which is then hydrolyzed to obtain one type of suitable polyoxyalkyleneamine.



The other type of suitable polyoxyalkyleneamines can be prepared by reactions of terminal hydroxyl groups of homopolymers of ethylene

oxide or copolymers of ethylene oxide and monosubstituted ethylene oxide with diisocyanates followed by hydrolysis of the terminal isocyanate groups to amines.



Preferred types of polyoxyalkyleneamines are those derived from reactions of diisocyanates with homopolymers of ethylene oxide or copolymers of ethylene oxide and propylene oxide. Preferred copolymers of ethylene oxide and propylene oxide are those available as Pluronic™ and Pluronic™ R surfactants from BASF Corporation, Parsipanny, NJ. According to the BASF literature these Pluronic™ surfactants are block copolymers of ethylene oxide and propylene oxide with different molecular weight and amount of ethylene oxide and propylene oxide. Most preferred Pluronic™ surfactants for the preparation of suitable polyoxyalkyleneamines are Pluronic™ F88, F98 and F108.

The mono ether of polyoxyalkylene diol or polyoxyalkylene diol and diisocyanate are reacted in the presence of catalysts such as organotin compounds and tertiary amines. This reaction can be performed with or without organic solvents. Suitable organic solvents are those containing no reactive groups which can react with isocyanate groups. Examples of suitable solvents are ketones, esters, aromatic hydrocarbons, ethers, etc. Preferred solvents are acetone, methylethylketone, methylisobutylketone,

ethyl acetate, butyl acetate, toluene, xylene, and tetrahydrofuran. An excess of diisocyanate equal to or greater than two equivalents per equivalent of hydroxyl group is used. Due to bifunctional nature of the diisocyanate, in addition to the mono-adduct of diisocyanate, the reaction products for monoethers of polyoxyalkylene diol also contain the bis-adduct of mono ether of polyoxyalkylene diol as well as reactants namely mono ether of polyoxyalkylenediol and diisocyanate. However the reaction conditions chosen favor the formation of mono-adduct as major component of the product mixture. Due to bifunctional nature of the reactants, in addition to the adduct of diisocyanate and hydroxyl terminated polymers shown above, the reaction products for polyoxyalkylene diol also contain species with isocyanate and hydroxyl terminal groups, higher molecular weight adducts of diisocyanates and hydroxyl terminated polymers and the starting materials. However the reaction conditions chosen favor the formation of adduct shown above as major component of the product mixture.

The hydrolysis of isocyanate group containing mono-adduct is performed with water in the presence of a mineral acid such as hydrochloric acid. The acid salt of the amine terminated polyoxyalkyleneamine formed after hydrolysis is treated with a suitable base to generate the free amine form of the polyoxyalkyleneamine.

Suitable diisocyanates for the preparation of adducts include aliphatic, cycloaliphatic, or aromatic diisocyanates such as 1,6-

hexamethylene diisocyanate, bis(4-isocyanatocyclohexyl)methane, isophoronediiisocyanate, tolylenediisocyanate (available as mixture of 2,4- and 2,6-isomers) and meta-tetramethylxylenediisocyanate (m-TMXDI available from Cytec Industries).

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### The Polyepoxide

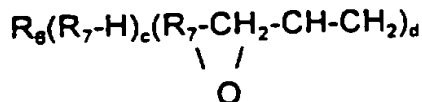
The polyepoxide reactant comprises one or more compounds each having a plurality of epoxide functional groups. The polyepoxide reactant has at least 2 epoxide groups present in the molecule, and may have as many as  
10 6 epoxide groups present in the molecule. Techniques to prepare suitable polyepoxide compounds are known in the art, and include reacting compounds having a plurality of hydroxyl groups with epichlorohydrin in the presence of a suitable catalyst. Both aliphatic and aromatic polyepoxides are suitable for this invention.

15

Suitable aliphatic polyepoxide compounds are commercially available from Henkel Corporation, Ambler Pennsylvania under the trademarks "Capcures Reg. TM" or "Photomers Reg. TM".

One representative class of aliphatic polyepoxide reactant according to the invention has the structural formula:

20



wherein

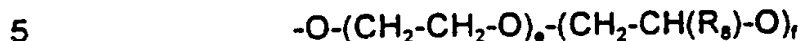
$R_6$  designates a linear, branched or cyclic aliphatic or alicyclic organic

radical having a valency equal to the sum of 'c' and 'd', where the sum of 'c' and 'd' is equal to or greater than 2 but no more than or equal to 6 and where 'd' is equal to or greater than 2 but less than or equal to 6. When the sum of 'c' and 'd' equals two (2),  $R_6$  designates a linear, branched or cyclic aliphatic or alicyclic divalent organic radical having from 2 to 14 carbon atoms, and specifically includes the hydrocarbon portions of the dihydric alcohols ethylene glycol, butylene glycol, hexylene glycol, decanediol and dodecanediol which remain after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals three (3),  $R_6$  designates a linear, branched or cyclic aliphatic or alicyclic trivalent organic radical having from 3 to 14 carbon atoms, and specifically includes the hydrocarbon portions of the trihydric alcohols glycerol, 1,1,1-tris(hydroxymethyl)ethane, and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol which remain after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals four (4),  $R_6$  designates a linear, branched or cyclic aliphatic or alicyclic tetravalent organic radical having from 5 to 30 carbon atoms, and specifically includes the hydrocarbon portion of the tetrahydric alcohol pentaerythritol which remains after the hydroxyl groups have been removed, and when the sum of 'c' and 'd' equals five (5),  $R_6$  designates a linear, branched or cyclic aliphatic or alicyclic pentavalent organic radical having from 6 to 30 carbon atoms, and when the sum of 'c' and 'd' equals six (6),  $R_6$  designates a linear, branched or cyclic aliphatic or alicyclic hexavalent organic radical having from 8 to 30 carbon atoms, and specifically includes the hydrocarbon portion of the hexahydric



alcohol dipentaerythritol which remains after the hydroxyl groups have been removed, and

$R_7$  represents a divalent polyoxyalkylene chain having the structural formula:



wherein

$R_8$  is a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons,

'e' designates a number of ethoxy groups ( $CH_2-CH_2-O$ ),

10 'f' designates a number of monosubstituted ethoxy groups ( $CH_2-CH(R_8)-O$ ) where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'e' and 'f' is equal to or greater than 0 but less than or equal to 10, and where the sequence of ethoxy and  
15 monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups.

The most preferred aliphatic polyepoxide compound is the reaction product of pentaerythritol, propylene oxide and epichlorohydrin, having an  
20 epoxide equivalent weight (EEW) of about 230.

Suitable aromatic polyepoxides include those disclosed in co-pending application Docket M5553 entitled "Aqueous Self-Dispersible Epoxy Resin Based on Epoxy-Amine Adducts Containing Aromatic Polyepoxide" which is

filed concurrently herewith and incorporated herein by reference. These include epoxy novolac resins such as Araldite EPN 1138 and 1139, epoxy cresol novolac resins such as Araldite ECN 1235, 1273, 1280 and 1299, epoxy phenol novolac resins such as Araldite PV 720, epoxy resin 0510, Araldite MY 720 and 721, and Araldite PT 810 all of which are available from Ciba-Geigy. Tetrad C and Tetrad X resins available from Mitsubishi Gas Chemical Co. are also suitable for use in this invention.

### The Epoxy Resin

The epoxy resin used in the practice of this invention comprises one or more epoxy resins having two (2) or more epoxide groups and one (1) or more six-carbon aromatized rings present in the molecule, as represented by the structural formula:



wherein

$R_g$  represents a 'g' valent  $C_6$ - $C_{50}$  organic radical comprising at least one six-carbon aromatized ring (e.g. when g is 2,  $R_g$  can be  $-CH_2 - O - \text{phenyl} -$  or  $C(CH_3)_2 - \text{phenyl} - O - CH_2 -$  wherein  $\text{phenyl}$  represents a phenyl group), and 'g' is equal to or greater than 2 but less than or equal to 6.

Techniques to prepare such epoxy resins are known in the art, and include reacting compounds having 2 or more hydroxyl groups with epichlorohydrin in the presence of a suitable catalyst. Suitable epoxy resins

are commercially available from a variety of sources and include EPON (Reg. TM) epoxy resins from Shell Chemical Company, Houston, Texas, and DER (Reg. TM) or DEN (Reg. TM) epoxy resins from Dow Chemical Company, Midland, Michigan.

5           Examples of suitable epoxy resins are:

I) Polyglycidyl and poly(beta-methylglycidyl) esters obtainable by reacting a compound having at least two carboxy groups in the molecule with epichlorohydrin or beta-methyl-epichlorohydrin, respectively. The reaction is advantageously carried out in the presence of bases. Examples of aromatic  
10 polycarboxylic acids which may be used include, for example, phthalic acid, isophthalic acid or terephthalic acid.

II) Polyglycidyl or poly(beta-methylglycidyl) ethers obtainable by reacting a compound having at least two free phenolic hydroxy groups with epichlorohydrin or beta-methyl-epichlorohydrin, respectively, under alkaline  
15 conditions, or in the presence of an acid catalyst and with subsequent alkali treatment.

The epoxy compounds of this type may be derived from mononuclear phenols, such as, for example, resorcinol or hydroquinone; or they are based on polynuclear phenols, such as, for example, bis(4-hydroxyphenyl)methane,  
20 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane, and from novolacs obtainable by condensation of aldehydes, such as formaldehyde, acetaldehyde, chloral or

furfuraldehyde, with phenols, such as phenol, or with phenols that are substituted in the nucleus by halide atoms or C<sub>1</sub>-C<sub>18</sub> (preferably C<sub>1</sub>-C<sub>9</sub>) alkyl groups, such as, for example, 4-chlorophenol, 2-methylphenol or 4-tert-butylphenol, or by condensation with bisphenols, in the manner described  
5 above.

There are preferably used epoxy resins that have an epoxy content of from 2 to 10 equivalents/mole and that are glycidyl ethers or glycidyl esters of aromatic or alkylaromatic compounds. Especially preferred epoxy resins are polyglycidyl ethers of bisphenols, such as, for example, of 2,2-bis(4-  
10 hydroxyphenyl)propane (bisphenol A) or bis(4-hydroxyphenyl)methane (bisphenol F), or novolacs formed by reacting formaldehyde with a phenol. For reasons of cost and availability, the most preferred epoxy resins are polyglycidyl ethers based on bisphenol A.

Preferred epoxy resins have an epoxide equivalent weight of less than  
15 about 400 grams/equivalent, e.g. from about 100 grams/equivalent to about 350 grams/equivalent, more preferably from about 150 grams/equivalent to about 225 grams/equivalent, e.g. DER 331 available from Dow Chemical at about 182 grams/equivalent.

## 20 The Polyhydric Phenol

The polyhydric phenol reactant comprises one or more compounds each having a plurality of hydroxyl groups covalently bonded to one or more six-carbon aromatized rings. The polyhydric phenol reactant may contain

substituents such as alkyl, aryl, sulfido, sulfonyl, halo, and the like. The polyhydric phenol is represented by the structural formula:



5     wherein

$R_{10}$  represents an 'h' valent  $C_6$ - $C_{50}$  organic radical comprising at least one six-carbon aromatized ring, and 'h' represents a number of phenolic hydroxyl groups where 'h' is equal to or greater than 2 but less than or equal to 6.

10       Techniques to prepare suitable polyhydric phenol compounds are known in the art. Suitable polyhydric phenol compounds are commercially available from Dow Chemical Company, Midland Michigan, and Shell Chemical Company, Houston, Texas.

Illustrative of suitable polyhydric phenols are

15     2,2-bis(4-hydroxyphenyl)propane,     2,2-bis(3-bromo-4-hydroxyphenyl)-propane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis(3-chloro-4-hydroxyphenyl)propane,     bis(4-hydroxyphenyl)-methane,     bis(4-hydroxyphenyl)sulfone,     bis(4-hydroxyphenyl)sulfide,     resorcinol, hydroquinone, phenol-formaldehyde novolac resins, and the like. The most  
20     preferred dihydric phenols are 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and bis(4-hydroxyphenyl)methane (bisphenol F) for reasons of cost and availability.

### The Amine-Epoxy Adduct

The preparation of certain of the self-dispersing curable epoxy resins of the invention proceeds through an amine-epoxy adduct, where the amine-epoxy adduct is subsequently reacted with an epoxy resin and, optionally, a polyhydric phenol. The structure of the amine-epoxy adduct is a complex mixture dependent on the structures of the polyoxyalkyleneamine and the polyepoxide used in the preparation of the amine-epoxy adduct, as well as the relative ratio of the reactants.

### 10 The Self-Dispersing Curable Epoxy Resin

Certain of the self-dispersing curable epoxy resins of the invention are prepared by reacting an amine-epoxy adduct with a polyhydric phenol and an epoxy resin. The structure and composition of the self-dispersing curable epoxy resin will depend on the identity of the amine-epoxy adduct, the identity of the epoxy resin, the identity of the polyhydric phenol and the relative ratio of the reactants.

### Organic Cosolvents

20 The self-dispersing curable epoxy resin of the present invention may be combined with a non-reactive, organic cosolvent. The cosolvent serves to reduce the viscosity of the self-dispersing curable epoxy resin. Preferred organic cosolvents include the alkyl ethers of monohydric and dihydric

alcohols, where the alkyl group comprises  $C_1$ - $C_8$  linear or branched aliphatic or alicyclic chains. The choice of cosolvent can affect the pot-life of the self-dispersing curable epoxy resin. For example, for a given resin it may be possible to increase the pot-life by substituting for a cosolvent such as

5 Ektasolve EP (Eastman Chemicals) with one of the following cosolvents (the greater increase being obtained in order): 1-methoxy-2-propyl acetate, methyl n-amyl ketone, or dipropylene glycol n-butyl ether.

#### Reactive Diluents

The preferred stable aqueous epoxy resin dispersions of the present

10 invention are those which contain a water-immiscible  $C_8$ - $C_{20}$  aliphatic monoepoxide reactive diluent. The said monoepoxide component can contain alicyclic and aromatic structures, as well as halogen, sulfur, phosphorus, and other such heteroatoms. Suitable reactive diluents are available from CVC Specialty Chemicals, Inc., Cherry Hill, New Jersey.

15 Illustrative of monoepoxide reactive diluents are epoxidized unsaturated hydrocarbons such as decene and cyclohexene; glycidyl ethers of monohydric alcohols such as 2-ethylhexanol, dodecanol and eicosanol; glycidyl esters of monocarboxylic acids such as hexanoic acid; acetals of glycidaldehyde; and the like. The preferred reactive diluent is glycidyl ether

20 of monohydric  $C_8$ - $C_{10}$  aliphatic alcohols.

The presence of a water-immiscible  $C_8$ - $C_{20}$  aliphatic monoepoxide reactive diluent in an aqueous epoxy resin dispersion has significant beneficial effects in addition to modifying the viscosity of the dispersion. For

example, the said water-immiscible reactive diluent appears to coat the particles of epoxy resin solids and thereby provide the aqueous dispersion with improved shear, freeze-thaw resistance, shelf viscosity stability, and paint gloss.

- 5           Also, since the reactive diluent is epoxy functional, it becomes chemically bonded into the film which is formed during the subsequent room temperature curing of the aqueous dispersion composition after it has been blended with a curing agent and coated on a surface. The total quantity of reactive diluent contributes to the calculated proportion of non-volatiles in the
- 10          dispersion composition.

#### Preparation of the Self-Dispersing Curable Epoxy Resin

- In preparing certain of the self-dispersing curable epoxy resins of this invention, an amine-epoxy adduct is first prepared by combining the
- 15          polyoxyallyleneamine reactant and the polyepoxide reactant, heating the mixture slowly to about 130°C, holding the mixture at temperature for about 2.5 hours, and then discharging the amine-epoxy adduct from the reactor. The respective self-dispersing epoxy resin is prepared by combining the amine-epoxy adduct, the polyhydric phenol and the epoxy resin, and heating
- 20          the mixture in the presence of a catalyst, e.g., potassium hydroxide, triphenyl phosphine, benzyl dimethylamine and the like, to a temperature of about 150°C with stirring. An exothermic reaction will then occur, and cooling is applied to maintain the reaction temperature at about 150-160°C. The



mixture is maintained at about 160°C for about one hour subsequent to the conclusion of the exothermic reaction. If the reaction has not progressed to the desired degree of completion (as determined by the epoxide equivalent weight of the reaction product) the mixture is then heated to 190°C. The  
5 reaction is maintained at 190°C for about 15 minutes in order to drive the reaction to completion, then cooled to about 160°C whereupon a small amount of organic solvent is added prior to cooling and discharging the self-dispersing curable epoxy resin from the reactor.

In certain embodiments, the polyoxyalkyleneamine is reacted directly  
10 with the epoxy resin to prepare a self-dispersing curable epoxy resin. The conditions employed for such a reaction may be the similar to the conditions under which the amine-epoxy adduct is formed.

#### Preparation of an Aqueous Dispersion of the Self-Dispersing Curable Epoxy

##### 15 Resin

The aqueous epoxy dispersion of the invention is prepared by charging the self-dispersing curable epoxy resin, as a mixture with a organic cosolvent, to a reaction vessel, then heating the resin to about 50-100°C with stirring. Water is then mixed with the mixture of organic cosolvent and self-dispersing  
20 curable epoxy resin to form an aqueous pre-emulsion which will typically be a disperse oil phase having a larger particle size.

The particle size of the oil phase in the aqueous dispersion can be modified by physical techniques to reduce the particle size. The particle size

reduction is preferably accomplished by subjecting the aqueous dispersion to high shear, e.g. in a homogenizer such as that disclosed in U.S. Patent No. 4,533,254 (Cook et al.), the disclosure of which is incorporated herein by reference, and commercially available as MICROFLUIDIZER™ from  
5 Microfluidics Corporation, Newton, Massachusetts. Homogenizers as well as other equipment suitable for making aqueous dispersion of epoxy resins are discussed in W. C. Griffin, "Emulsions", Encyclopedia of Chemical Technology, Vol. 8, pp. 900-930 (Kirk-Othmer, eds., John Wiley & Sons, Inc., New York, New York, 3d ed., 1979), the disclosure of which is incorporated  
10 herein by reference. High shear mixers suitable for reducing particle size are further described in Wicks, Z.W., Jr., Jones, F.N., Pappas, S.P., Organic Coatings: Science and Technology. Volume II. Application, Properties and Performance, John Wiley & Sons, Inc., New York, 1994, pp. 42-45, the disclosure of which is incorporated herein by reference.

15       After reduction of the particle size, at least a portion of the organic cosolvent is removed. The organic cosolvent is removed by volatilizing the same from the mixture. This is an evaporative process that may be considered a distillation. Sufficient organic cosolvent should be removed so that the aqueous dispersion will be low in volatile organic compounds, and  
20       preferably essentially free of such compounds.

The removal of the organic cosolvent will be facilitated by subjecting an agitated dispersion to elevated temperatures and/or reduced pressures, e.g. a vacuum distillation. The precise temperature and pressure employed

to effect removal of the organic cosolvent will, of course, depend upon the volatility of the organic cosolvent chosen, but temperatures that will cause degradation or polymerization of the resin should be avoided. Distillation is discussed in E. Hafslund, "Distillation", Encyclopedia of Chemical Technology, vol. 7, pp. 849-891 (Kirk-Othmer, eds. John Wiley & Sons, N.Y., 3d ed. 1979) and evaporation is discussed in F. Standiford, "Evaporation", Encyclopedia of Chemical Technology, vol. 9, pp. 472-493 (Kirk-Othmer, eds. John Wiley & Sons, N.Y., 3d ed. 1980), the disclosures of which are incorporated by reference.

10       The aqueous dispersion of self-dispersing resin will typically exhibit excellent chemical and physical stability over an extended shelf-life, e.g. of from five to six months. As an example of the chemical stability, the epoxide equivalent weight (EEW) of the aqueous dispersion of self-dispersing resin should remain essentially constant, e.g. should show no trend of increasing molecular weight, over a period of at least one month from the preparation of the aqueous dispersion.

20       Epoxide equivalent weight can be determined by differential titration with perchloric acid using crystal violet as an indicator (e.g. a first sample is titrated with 0.1 N perchloric acid to an endpoint that shows the first sight of green color from the crystal violet indicator, the amine equivalent weight of the dispersion is calculated from this titration, a second sample is mixed with excess tetraethylammonium bromide and titrated with 0.1 N perchloric acid to a green endpoint that persists for at least 30 seconds, total epoxide and

amine equivalents are calculated from this titration, and the epoxide equivalent weight is calculated as the difference).

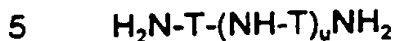
As an example of physical stability, the resin should not display layer formation for a period of at least one month from the preparation of the aqueous dispersion, i.e. there should be no formation of a macro-observable water phase as a layer separate from the dispersed resin phase.

Coating Compositions Comprising an Aqueous Dispersion of the Self-Dispersing Curable Epoxy Resin

The coating composition of the invention is prepared by combining the aqueous epoxy dispersion with a suitable hardening agent. The coatings are tack free after 45 minutes and have excellent film properties. An aqueous epoxy resin paint composition of the present invention may further contain additives conventionally employed in coating technology, such as organic pigments, inorganic pigments, surfactants, thickeners, and the like.

A room temperature curable water-borne coating composition is prepared by admixing a stable epoxy dispersion composition as described above with an epoxy-interacting curing vehicle, such as a polyamine curing agent. The ratio of active amino hydrogens to epoxy groups in the admixture is in the range of from 0.5:1 to 2:1 and, preferably, is in the range between about 0.8:1 to 1.5:1. For purposes of industrial maintenance paint compositions, the amino hydrogens must be sufficiently reactive to effect crosslinking interaction with the epoxy groups at ambient temperatures.

Suitable polyamine curing agents are those which are soluble or dispersible in water and which contain more than 2 active hydrogen atoms per molecule. Examples of such curing agents are alkylene polyamines represented by the formula:



wherein 'T' is an alkylene radical containing 2 to 6 carbon atoms and 'u' is equal to or greater than zero (0) but less than or equal to five (5). Such alkylene polyamines include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene  
10     diamine, dibutylene triamine, hexamethylene diamine, and the like.

Other polyamine curing agents that can be employed in the practice of this invention are the polyamido amines, which are reaction products of alkylene polyamines and fatty acids. Such polyamidoamines are well known in the art and are described in U.S. Pat. Nos. 2,705,223, 2,811,495 and  
15     2,899,397, which patents are hereby incorporated by reference. Other polyamine curing agents are the adducts of polyamines and epoxy compounds such as those described in U.S. Pat. Nos. 2,651,589, 2,864,775 and 4,116,900, which patents are hereby incorporated by reference.

Examples of useful curing agents also include those disclosed in U.S.  
20     patent application Serial No. 08/085,861, filed June 30, 1993, entitled "Curing Agents for Aqueous Epoxy Resins", by Jason Chou et al., the disclosure of which is incorporated herein by reference. These epoxy curing agents comprise the reaction product of reactants consisting essentially of an

alkylene polyamine having less than about 12 carbon atoms, an aromatic mono-glycidyl ether having less than about 18 carbon atoms, and a diglycidyl ether of an aromatic diol having an average degree of oligomerization of less than about 3.5, wherein the ratio of primary amine equivalents of said  
5 alkylene polyamine to the total epoxide equivalents of said aromatic glycidyl ether and said diglycidyl ether of an aromatic diol is not essentially less than one, and the ratio of epoxide equivalents of said aromatic mono-glycidyl ether to epoxide equivalents of said diglycidyl ether of an aromatic diol is greater than one.

10 In addition to the amine curing agent, a curing accelerator can be included in the coating composition. Such an accelerator will serve to reduce the time for the coating to become tack-free. Useful accelerators for amine curing agents include tertiary amines, e.g. N,N'-bis(dimethyl-amino-propyl) urea.

15 Other curing agents can be used in the composition of this invention, particularly when the coatings made from the compositions are heated to effect a cure. Examples of such additional curing agents are the aminoplast and phenoplast resins. Suitable aminoplast resins are the reaction products of ureas and melamines with aldehydes further etherified in some cases with  
20 an alcohol. Examples of aminoplast resin components are urea, ethylene urea, thiourea, melamine, benzoguanamine and acetoguanamine. Aldehydes include formaldehyde, acetaldehyde and propionaldehyde. The aminoplast resins can be used in the alkylol form but, preferably, are utilized in the ether

form wherein the etherifying agent is a monohydric alcohol containing from 1 to 8 carbon atoms. Examples of suitable aminoplast resins are methylol urea, dimethoxymethylol urea, butylated polymeric urea-formaldehyde resins, hexamethoxymethyl melamine, methylated polymeric melamine-formaldehyde resins and butylated polymeric melamine-formaldehyde resins.

Phenoplast resins are the reaction products of phenols and aldehydes which contain reactive methylol groups. These compositions can be monomeric or polymeric in nature depending on the molar ratio of phenol to aldehyde used in the initial condensation reaction. Examples of suitable phenols are phenol, o, m or p-cresol, 2,4-xyleneol, 3,4-xyleneol, 2,5-xyleneol, cardanol, p-tert-butyl phenol, and the like. Useful aldehydes are formaldehyde, acetaldehyde and propionaldehyde. Particularly useful phenoplast resins are polymethylol phenols wherein the phenolic group is etherified with an alkyl, e.g., methyl or ethyl, group.

Other epoxy resin curing agents may also be useful, e.g. catalytic curing agents: Lewis bases (such as tertiary amines), Lewis acids (such as boron trifluoride), cationic curing agents (such as aryldiazonium salts, diaryliodonium salts, onium salts of Group VIa elements, especially sulfur) and reactive curing agents: mercaptans, isocyanates, carboxylic acids, and acid anhydrides. Curing agents for epoxy resins in general are discussed in the Encyclopedia of Polymer Science and Engineering, vol. 6, pp. 340-361 (John Wiley & Sons, Inc., N.Y., N.Y., 1986), the disclosure of which is incorporated by reference.

The following examples are further illustrative of the present invention. The reactants and other specific ingredients are presented as being typical, and various modifications can be derived in view of the foregoing disclosure within the scope of the invention.

5

### EXAMPLES

#### Example 1

Polyoxyalkyleneamine from Poly(ethylene glycol) Monomethyl Ether of molecular weight 550 (PEGMME-550) and Tolylenediisocyanate (TDI). A

10 suitable reaction set-up consists of a four-neck round-bottom flask equipped with stirrer, condenser, heating mantle with means to monitor and control temperature such as Jack-o-matic™ with on-off controller, addition funnel and means for maintaining nitrogen atmosphere. The reaction flask is charged with 55 g (0.1 mole) of PEGMME-550, (available  
15 from Polysciences, Inc., Warrington, PA dried by vacuum distillation or with suitable drying agents to remove water if necessary) and 0.2 g of dibutyl tin dilaurate (Aldrich Chemical Co.). Stirring is started and addition of 17.4 g of Mondur TDS (TDI, available from Miles, 0.1 mole) is made dropwise over 1 h. An increase in temperature is observed and cooling is  
20 applied to the reaction flask if necessary to keep the temperature below  $65 \pm 5$  C. After addition of Mondur TDS is complete reaction is continued at  $65 \pm 5$  C until isocyanate value of the reaction mixture is determined to be  $6.1 \pm 0.6$  % by weight (determined by titration per ASTM D-2572-87).



Heating is stopped and reaction mixture is cooled with ice-water bath and 125 ml of 8N hydrochloric acid is added slowly with stirring. The cooling bath is removed and the reaction mixture is heated on a steam bath with stirring until evolution of carbon dioxide is stopped. The reaction mixture is  
5 refluxed for 10 minutes and then allowed to cool. Addition of 2N sodium hydroxide is made with cooling to a pH of 12. The reaction mixture is extracted with three 250 ml portion of diethyl ether, the ether extracts are dried with anhydrous magnesium sulfate and then subjected to rotary evaporation to obtain the polyoxyalkyleneamine with a calculated amine  
10 value of  $1.43 \pm 0.2$  milliequiv./g.

#### Example 2

Polyoxyalkyleneamine from PEGMME-1900 and TDI. This polyoxyalkyleneamine is prepared in a manner similar to that of Example 1 except 190 g of poly(ethylene glycol) monomethyl ether of molecular  
15 weight 1900 (available from Polysciences, Inc.) is used. Calculated amine value of this polyoxyalkyleneamine is  $0.49 \pm 0.1$  milliequiv./g.

#### Example 3

Polyoxyalkyleneamine from PEGMME-550 and Isophoronediiisocyanate (IPDI). This polyoxyalkyleneamine is prepared similar to that of example 1 except 22.2 g (0.1 mole) of isophorone diisocyanate (Vestanat IPDI, Huels  
20 America) is used in place of TDI. Calculated amine value of this polyoxyalkyleneamine is  $1.34 \pm 0.2$  milliequiv./g.

Example 4

Polyoxyalkyleneamine from PEGMME-1900 and IPDI. This

polyoxyalkyleneamine is prepared similar to that of Example 2 except 22.2 g IPDI is used in place of TDI. Calculated amine value of this

5 polyoxyalkyleneamine is  $0.48 \pm 0.1$  milliequiv./g.

Example 5

Epoxy Functional Dispersant from Polyoxyalkyleneamine of Example 1.

Reaction set-up for this example is similar to that for Example 1. Reaction  
10 flask is charged with 48.3 g of the polyoxyalkyleneamine of Example 1 and  
51.7 g Capcure 711 (multifunctional polyglycidyl ether of EEW 230  
available from Henkel Corporation) at room temperature with stirring under  
an atmosphere of nitrogen. The reaction mixture is heated to  $125 \pm 5$  C with  
stirring and held at this temperature until EEW of the reaction mixture is  
15 determined to be  $1080 \pm 200$  (determined by titration with perchloric acid  
per ASTM D-1652-88, a correction is needed for the presence of amine  
groups in the polyoxyalkyleneamine). Heating is stopped and the product  
is discharged.

20 Example 6

Self-dispersible Epoxy Resin of EEW 550 from the Dispersant of Example

5. Reaction set-up for this example is similar to that for Example 1.

Reaction flask is charged with 245 g dispersant of Example 5, 593 g

D.E.R. 331 (epoxy resin of EEW 195 available from Dow Chemical Co.), 162 g BPA-157 (bis-phenol A available from Shell Chemical Co.) and 1 g ethyltriphenylphosphonium iodide (ETPPI) under an atmosphere of nitrogen. Stirring is started and the reaction mixture is heated slowly to 160 $\pm$ 5 C. An exothermic reaction takes place and cooling is applied if necessary to maintain reaction temperature in this range. Reaction is continued until EEW of the product is determined to be 550 $\pm$ 50 (titration with perchloric acid per ASTM D-1652-88, corrected for amine value). Heating is stopped and addition of 110 g ethylene glycol propyl ether (Ektasolve EP, Eastman Chemical Co.) is made slowly. After addition of solvent is complete and reaction temperature is 90 $\pm$ 5 C, addition of 213 g of de-ionized water is made slowly. Heating is applied if necessary so that the reaction temperature does not fall below 75 $\pm$ 5 C at the completion of water addition. After water has been added and mixed in, the reaction temperature is allowed to drop to 50 $\pm$ 5 C and then the sample is tested for inversion from water-in-oil to oil-in-water phase. This is evident when a small amount of the product is found to mix readily with water. After inversion addition of 496 g of de-ionized water is made slowly with stirring at 50 $\pm$ 5 C and then the product is cooled to below 40 C and discharged. A dispersion with calculated solids of 55% is obtained in this manner which can be used for the formulation of coatings described below.

Example 7Self-dispersible Epoxy Resin with EEW 1800 from the Dispersant of

Example 5. Reaction set-up for this example is similar to that for Example

1. Reaction flask is charged with 216 g dispersant of Example 5, 523 g
- 5 D.E.R. 331 (epoxy resin of EEW 195 available from Dow Chemical Co.), 261 g of BPA-157 (bis-phenol A available from Shell Chemical Co.) and 1 g ETPPI under an atmosphere of nitrogen. Stirring is started and the reaction mixture is heated slowly to  $160 \pm 5$  C. An exothermic reaction takes place and cooling is applied if necessary to maintain reaction temperature
- 10 in this range. Reaction is continued until EEW of the product is determined to be  $1800 \pm 200$  (titration with perchloric acid per ASTM D-1652-88, corrected for amine value). Heating is stopped and addition of 250 g ethylene glycol propyl ether (Ektasolve EP, Eastman Chemical Co.) is made slowly. After addition of solvent is complete and reaction
- 15 temperature is  $90 \pm 5$  C, addition of 171 g of de-ionized water is made slowly. Heating is applied if necessary so that the reaction temperature does not fall below  $65 \pm 5$  C at the completion of water addition. After water has been added and mixed in, the reaction temperature is allowed to drop to  $50 \pm 5$  C and then the sample is tested for inversion from water-in-oil to
- 20 oil-in-water phase. This is evident when a small amount of the product is found to mix readily with water. After inversion addition of 398 g of de-ionized water is made slowly with stirring at  $50 \pm 5$  C and then the product is cooled to below 40 C and discharged. A dispersion with calculated solids

of 55% is obtained in this manner which can be used for the formulation of coatings and described below.

#### Example 8

##### Epoxy Functional Dispersant from the Polyoxyalkyleneamine of Example

- 5     2. Preparation of this dispersant is made similar to that of Example 5 using 73.2 g of the polyoxyalkyleneamine of Example 2 and 26.8 g Capcure 711. This polyoxyalkyleneamine has EEW of  $2100 \pm 400$  (after correction for amine value).

#### 10     Example 9

##### Self-dispersible Epoxy Resin of EEW 550 from the Dispersant of Example

8. This epoxy resin is prepared similar to that of Example 6 using 151 g dispersant of Example 8, 655 g D.E.R. 331, 194 g BPA-157 and 1 g ETPPI. Amounts of solvent and water are similar to those of Example 6.

15

#### Example 10

##### Preparation of a Self-dispersible Epoxy Resin of EEW 1800 from the

Dispersant of Example 8. This epoxy resin is prepared similar to that of Example 7 using 100 g dispersant of Example 8, 603 g D.E.R. 331, 296 g

- 20     BPA-157 and 1 g ETPPI. Amounts of solvent and water are similar to those used in Example 7.

#### Example 11

##### Epoxy Functional Dispersant from Polyoxyalkyleneamine of Example 3.

Preparation of this dispersant is similar to that of Example 5 using 49.9 g Capcure 711 and 50.1 g polyoxyalkyleneamine of Example 3. EEW of reaction product is  $1120 \pm 200$  (after correction for amine value).

5     Example 12

Self-dispersible Epoxy Resin of EEW 550 from Dispersant of Example 11.

The epoxy resin is prepared similar to that of Example 6 using 251 g dispersant of Example 11, 588 g D.E.R. 331, 161 g BPA-157 and 1 g ETPPI. Amounts of solvent and water are similar to those used in Example

10     6.

Example 13

Self-dispersible Epoxy Resin of EEW 1800 from Dispersant of Example

11. This epoxy resin is prepared similar to that of Example 7 using 221 g

15     Dispersant of Example 11, 519 g D.E.R. 331, 259 g BPA-157 and 1 g ETPPI. Amounts of solvent and water are similar to those used for Example 7.

Example 14

20     Epoxy Functional Dispersant from Polyoxyalkyleneamine of Example 4.

Preparation of this dispersant is made similar to that for Example 5 using 26.4 g Capcure 711 and 73.6 g polyoxyalkyleneamine of Example 4. EEW of the dispersant is  $2100 \pm 400$ .

### Example 15

#### Self-dispersible Epoxy Resin of EEW 550 from Dispersant of Example 14.

The epoxy resin is prepared similar to that of Example 6 using 153 g dispersant of Example 14, 654 g D.E.R. 331, 193 g BPA-157 and 1 g  
5 ETPPI. Amounts of solvent and water are similar to those for Example 6.

### Example 16

#### Self-dispersible Epoxy Resin of EEW 1800 from Dispersant of Example

14. This epoxy resin is prepared similar to that of Example 7 using 102 g  
10 dispersant of Example 14, 603 g D.E.R. 331, 296 g BPA-157 and 1 g ETPPI. Amounts of solvent and water are similar to those for Example 7.

### Example 17.

#### Preparation of a Polvoxyalkyleneamine from Polyethyleneglycol of

15 Molecular Weight 1,500. A suitable reaction set-up for this Example is similar to that for Example 1. The reaction flask is charged with 150 g (0.1 mole) of polyethyleneglycol (mol. Wt. 1,500, available from Polysciences, Inc., Warrington, PA, calculated hydroxyl value 75 mg of KOH/g, dried by vacuum distillation or suitable drying agents), 100 mL of dry toluene and  
20 0.2 g dibutyl tin dilaurate. The reaction mixture is heated to 50° C to melt the polyethyleneglycol and addition of 48.8 g isophoronediiisocyanate (0.22 mole, available from Huels America under the trade name Vestanat IPDI) is made slowly over 1 h. Cooling or heating is applied as necessary to

maintain reaction temperature at  $60 \pm 5^\circ \text{C}$  during the addition. After addition of diisocyanate is complete, reaction is continued at  $60 \pm 5^\circ \text{C}$  until isocyanate content of the reaction mixture (determined by titration with dibutylamine per ASTM D-2572-87) is found to be  $5.3 \pm 0.5\%$  by weight (on solids). Heating is stopped and reaction mixture is cooled with ice-water bath and 125 mL of 8N hydrochloric acid is added slowly with stirring. The cooling bath is removed and the reaction mixture is heated on a steam bath with stirring until evolution of carbon dioxide is stopped. The reaction mixture is refluxed for 10 minutes and then allowed to cool. Addition of 2N sodium hydroxide is made with cooling to a pH of 12. The reaction mixture is then subjected to vacuum distillation to remove volatile organics and water and filtered to obtain a polyoxyalkyleneamine with calculated amine value of  $1.0 \pm 0.1$  milliequivalent per g.

#### Example 18

##### 15     Self-dispersible Epoxy Resin from Polvoxyalkyleneamine of Example 17.

The reaction set-up for this Example is similar to the one used for Example 1. The reaction flask is charged with 56.8 g (0.24 equiv.) of Capcure 711 (available from Henkel Corporation) and 43.2 g (0.09 hydrogen equiv.) polyoxyalkyleneamine of Example 17. Contents of the flask are heated with stirring to  $95^\circ \text{C}$ . After 1.5 h of reaction at this temperature epoxy-amine adduct of EEW 648 (after correction for amine content) is obtained. In a separate reaction flask, 206.7 g (1.06 equiv.) of D.E.R. 331 (available from Dow Chemical Co.), 61.76 g (0.54 equiv.) of bis-phenol A (available



from Shell Chemical Co.), 131.6 g (0.2 equiv.) of the amine-epoxy adduct prepared above and 0.7 g of triphenylphosphine catalyst are heated with stirring to 160° C. Care is exercised to control the exotherm by application of heating and cooling as necessary. The reaction mixture is held at 160° C for 1.5 h and then heating is stopped. Addition of 54.5 g Ektasolve EP (available from Eastman Chemical Co.) is made with cooling the reaction mixture to 85° C and then addition of 130 g de-ionized water is made with stirring in 1.5 h. The reaction mixture is then cooled with stirring until it is found to be inverted from water-in-oil phase to oil-in-water phase as evident by its ready dispersion in water. After that 130 g of de-ionized water is added over 1 h. After complete addition of water the product is heated to 55° C and held at that temperature for 1 h. A dispersion of epoxy resin with EEW 560 (after correction for amine content), and 62% solids is obtained.

15

### Example 19

#### Preparation of a Polvoxyalkyleneamine from a Copolymer of Ethylene Oxide and Propylene Oxide (Pluronic F88) of Molecular Weight 1,5000. A

suitable reaction set-up for this Example is similar to that for Example 1.

20 The reaction flask is charged with 228 g (0.02 mole) of Pluronic F88 (mol. Wt. 11,400, available from BASF, calculated hydroxyl value 10 mg of KOH/g, dried by vacuum distillation or suitable drying agents), 100 mL of dry toluene and 0.2 g dibutyl tin dilaurate. The reaction mixture is heated

to 60° C to melt Pluronic F88 and addition of 9.8 g isophoronediiisocyanate (0.044 mole, available from Huels America under the trade name Vestanat IPDI) is made slowly over 1 h. Cooling or heating is applied as necessary to maintain reaction temperature of 60+5° C during the addition. After

5 addition of diisocyanate is complete, reaction is continued at 60+5° C until isocyanate content of the reaction mixture (determined by titration with dibutylamine per ASTM D-2572-87) is found to be 1.0+0.1% by weight (on solids) Heating is stopped and reaction mixture is cooled with ice-water bath and 125 mL of 8N hydrochloric acid is added slowly with stirring. The

10 cooling bath is removed and the reaction mixture is heated on a steam bath with stirring until evolution of carbon dioxide is stopped. The reaction mixture is refluxed for 10 minutes and then allowed to cool. Addition of 2N sodium hydroxide is made with cooling to a pH of 12. The reaction mixture is then subjected to vacuum distillation to remove volatile organics and

15 water and filtered to obtain a polyoxyalkyleneamine with calculated amine value of 0.17+0.02 milliequivalent per g.

### Example 20

#### Self Dispersible Epoxy Resin from Polyoxyalkyleneamine of Example 19.

20 The reaction set-up for this Example is similar to the one used for Example 1. The reaction flask is charged with 17.6 g (0.08 equiv.) of Capcure 711 (available from Henkel Corporation) and 82.4 g (0.03 hydrogen equiv.) polyoxyalkyleneamine of Example 5. Contents of the flask are heated with

stirring to 95° C. After 1.5 h of reaction at this temperature epoxy-amine adduct of EEW 2100

(after correction for amine content)

is obtained. In a separate reaction flask, 222.4 g (1.14 equiv.) of D.E.R.

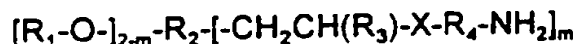
5 331 (available from Dow Chemical Co.), 63.2 g (0.36 equiv.) of bis-phenol A (available from Shell Chemical Co.), 114.4 g (0.05 equiv.) of the amine-epoxy adduct prepared above and 0.7 g of triphenylphosphine catalyst are heated with stirring to 160° C. Care is exercised to control the exotherm by application of heating and cooling as necessary. The reaction mixture is  
10 held at 160° C for 1.5 h and then heating is stopped. Addition of 54.5 g Ektasolve EP (available from Eastman Chemical Co.) is made with cooling the reaction mixture to 85° C and then addition of 130 g de-ionized water is made with stirring in 1.5 h. The reaction mixture is then cooled with stirring until the reaction mixture is found to be inverted from water-in-oil phase to  
15 oil-in-water phase as evident by its ready dispersion in water. After that 130 g of de-ionized water is added over 1 h. After complete addition of water the product is heated to 55° C and held at that temperature for 1 h. A dispersion of epoxy resin with EEW 630 (after correction for amine content). and 62% solids is obtained.

20 The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be

regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

We claim:

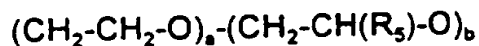
1. A self-dispersing curable epoxy resin composition comprising the addition product of reactants comprising (a) 1.0 reactive equivalent of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents of a polyhydric phenol, and (c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct comprising the addition product of reactants comprising 1.0 reactive equivalent of a polyepoxide and from about 0.3 to 0.9 reactive equivalents of a polyoxyalkyleneamine having the structural formula:



10 wherein:

$R_1$  designates a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_{12}$  aliphatic, alicyclic or aromatic hydrocarbons, and

$R_2$  represents a polyoxyalkylene chain having the structural formula:



15 wherein:

$R_5$  is a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons,

'a' designates a number of ethoxy groups ( $CH_2-CH_2-O$ ),

'b' designates a number of monosubstituted ethoxy groups ( $CH_2-CH(R_5)O$ )

20 where the substitution of one monosubstituted ethoxy group is independent from the substitution of any other monosubstituted ethoxy group in the polyoxyalkylene chain, the sum of 'a' and 'b' is equal to or greater than 10 but less than or equal to 200, and where the sequence of ethoxy and

monosubstituted ethoxy groups within a polyoxyalkylene chain may be completely random and/or there may be blocks of ethoxy and/or monosubstituted ethoxy groups, and where the ratio of a:b is greater than 1:1.

- 5             $R_3$  designates H or a monovalent organic radical selected from the group consisting of  $C_1$  to  $C_4$  aliphatic hydrocarbons.

$R_4$  designates aliphatic, cycloaliphatic or aromatic radical containing 6 to 18 carbon atoms and X is  $OC(O)NH$ .

And m is equal to 1 or 2.

- 10           2.        A composition as claimed in claim 1 wherein said epoxy resin has an epoxide equivalent weight of less than about 400 grams/equivalent.

3.        A composition as claimed in claim 1 wherein said epoxy resin has an epoxide equivalent weight of from about 100 grams/equivalent to about 350 grams/equivalent.

- 15           4.        A composition as claimed in claim 1 wherein said epoxy resin has an epoxide equivalent weight of from about 150 grams/equivalent to about 225 grams/equivalent.

5.        A composition as claimed in claim 1 wherein said polyhydric phenol is present in a ratio of from about 0.45 to about 0.90 reactive  
20        equivalents to said 1.0 reactive equivalents of said epoxy resin.

6.        A composition as claimed in claim 1 wherein said polyoxyalkyleneamine is comprised of ethyleneoxy groups.

7.        A composition as claimed in claim 1 wherein from about 43%

to about 95% by weight of the oxyalkylene groups of said polyoxyalkyleneamine are ethyleneoxy groups.

8. A composition as claimed in claim 1 further comprising between about 20-80 weight percent of a solvent phase comprising between 50 and  
5 100 weight percent water and between 0 and 50 weight percent of organic cosolvent, and about 80-20 weight percent of said self-dispersing curable epoxy dispersion composition.

9. A composition as claimed in claim 1 wherein 0.005 to 0.025 reactive equivalents of said amine-epoxy adduct are reacted per equivalent  
10 of said epoxy resin.

10. A composition as claimed in claim 1 wherein 0.005 to 0.015 reactive equivalents of said amine-epoxy adduct are reacted per equivalent of said epoxy resin.

11. A self-dispersing curable epoxy resin composition prepared by  
15 the process of reacting (a) 1.0 reactive equivalents of an epoxy resin, (b) from about 0.01 to 1.0 reactive equivalents of a polyhydric phenol, and (c) from about 0.005 to 0.5 reactive equivalents of an amine-epoxy adduct comprising the addition product of reactants comprising 1.0 reactive equivalent of a polyepoxide and from about 0.3 to 0.9 reactive equivalents of a  
20 polyoxyalkyleneamine as defined in claim 1.

12. An aqueous dispersion comprising a self-dispersing epoxy resin, wherein the self-dispersing epoxy resin is prepared by the steps comprising:

(a) preparing an amine-epoxy adduct by contacting a polyoxyalkyleneamine, as defined in claim 1 and a polyepoxide, where the ratio of the reactive equivalents of the polyoxyalkyleneamine and the polyepoxide is in the range from about 0.3:1 to 0.9:1, and

5 (b) contacting the amine-epoxy adduct with a polyhydric phenol and an epoxy resin, where the ratio of the reactive equivalents of the polyhydric phenol and the epoxy resin is in the range from about 0.1:1 to about 1.0:1, and where the ratio of the reactive equivalents of the amine-epoxy adduct and the epoxy resin is in the range from about 0.005:1 to about 0.5:1.

10 13. A composition as claimed in claim 13 further comprising (1) between about 20-80 weight percent of a solvent phase comprising between 50 and 100 weight percent water and between 0 and 50 weight percent of organic cosolvent, and about 80-20 weight percent of said self-dispersing curable epoxy dispersion composition.

15 14. A coating composition comprising a cured self-dispersing epoxy resin as defined in claim 1.

15. A process for preparing a self-dispersing curable epoxy resin dispersion, said process comprising:

20 reducing the particle size of a mixture comprised of a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine, water and an organic cosolvent and

removing at least a major amount of said organic cosolvent from said mixture after said reducing.



16. A process as claimed in claim 15 wherein the self-dispersing curable epoxy resin composition is as claimed in claim 1.

17. A process as claimed in claim 15 wherein the self-dispersing curable epoxy resin composition is as claimed in claim 11.

5 18. A process as claimed in claim 16 wherein said reactive equivalents of said polyhydric phenol are from about 0.4 to about 0.6 reactive equivalents.

19. A process as claimed in claim 16 wherein said reactive equivalents of said polyhydric phenol are from about 0.65 to about 0.95  
10 reactive equivalents.

20. A process as claimed in claim 15 further comprising preparing said self-dispersing curable epoxy resin composition by reacting an epoxy resin with a polyoxyalkyleneamine, as defined in claim 1 having a molecular weight of from about 3,000 to about 15,000 in a ratio of about 0.001 to 0.060  
15 reactive equivalents of said polyoxyalkyleneamine, to about 1.0 reactive equivalents of epoxy resin.

21. A process as claimed in claim 15 wherein said organic cosolvent is a methyl lower-alkyl ketones, wherein said lower alkyl group has from 1 to 3 carbon atoms.

20 22. A process as claimed in claim 15 wherein the amounts of said resin, water and organic cosolvent will range between about 20% to about 50% each by weight of said mixture.

23. A process as claimed in claim 15 wherein the amount of said

resin in said mixture is from about 35% to about 45% by weight of said mixture and the amounts of water and organic cosolvent each range from about 25% to about 35% of said mixtures.

24. A process as claimed in claim 15 wherein said removing is by  
5 vacuum distillation.

25. A process as claimed in claim 15 wherein said removing is effective to reduce the amount of organic cosolvent in said mixture to less than 1% by weight of said mixture.

26. A process as claimed in claim 15 wherein said removing is  
10 effective to reduce the amount of organic cosolvent in said mixture to less than 0.1% by weight of said mixture.

27. A process as claimed in claim 15 wherein said reducing is effective to reduce the mean particle size of the oil phase in said mixture to less than about 3 microns.

28. A process as claimed in claim 15 wherein said reducing is  
15 effective to reduce the mean particle size of the oil phase in said mixture to from about 0.1 microns to about 3 microns.

29. An aqueous dispersion comprising a self-dispersing epoxy resin prepared by the steps comprising:

20 (a) preparing a self-dispersing a self-dispersing curable epoxy resin based on a polyoxyalkyleneamine as defined in claim 1,

(b) reducing the particle size of a mixture comprised of said self-dispersing curable epoxy resin, water and an organic cosolvent, and

(c) removing at least a major amount of said organic cosolvent from said mixture after said reducing.

30. An aqueous dispersion as claimed in claim 29 wherein said preparing comprises first preparing an amine-epoxy adduct by contacting a polyoxyalkyleneamine and a polyepoxide, where the ratio of the reactive equivalents of the polyoxyalkyleneamine and the polyepoxide is in the range from about 0.3:1 to 0.9:1, and then contacting said amine-epoxy adduct with a polyhydric phenol and an epoxy resin, where the ratio of the reactive equivalents of the polyhydric phenol and epoxy resin is in the range from about 0.01:1 to about 1.0:1, and where the ratio of the reactive equivalents of the amine-epoxy adduct and the epoxy resin is in the range from about 0.005:1 to about 0.5:1 to produce a self-dispersing curable epoxy resin.

# INTERNATIONAL SEARCH REPORT

national application No.  
PCT/US95/16013

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08L 63/00, 63/02

US CL :523/404, 414, 415, 417, 420

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/404, 414, 415, 417, 420

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,262,465 (OTT ET AL) 16 November 1993, see the abstract and claims.	1-30



Further documents are listed in the continuation of Box C.



See patent family annex.

\*

Special categories of cited documents:

\*A\*

document defining the general state of the art which is not considered to be of particular relevance

\*E\*

earlier document published on or after the international filing date

\*L\*

document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\*

document referring to an oral disclosure, use, exhibition or other means

\*P\*

document published prior to the international filing date but later than the priority date claimed

\*T\*

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\*

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\*

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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document member of the same patent family

Date of the actual completion of the international search

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